Chapter 3 **Removing Nickel from Wastewater**

The Removal of Nickel using the OLI Studio

This tour of the OLI Studio is based upon a typical wastewater treatment problem, removal of a trace heavy metal ion (nickel) from a stream in which the presence of another chemical (cyanide) significantly alters the treatment strategy. In this case, we are considering precipitation as an approach to removal of nickel.

In this application, a user is discharging a wastewater that contains nickel ion at a concentration of 0.002 moles/Kg H_2O. The existing treatment strategy is to precipitate the nickel ion as Nickel Hydroxide ($Ni(OH)_2$). The soluble nickel remaining after precipitation is less than 1 ppm, which is a design specification.

During the course the plant operation, some cyanide ion is inadvertently added to the waste stream. The soluble nickel is now in excess of 1ppm. Sulfide salts were then added to hopefully precipitate the nickel and once again achieve the design specification.

The power of OLI Studio becomes apparent when we are seeking to study the chemistry of individual streams.

We will illustrate the steps necessary to solve these problems in great detail. This section is designed to be used as a guide for future reference.

How to run the tour?

In this tour, and all subsequent tours, when action is required by the user, the instruction will be in ***Bold and Italic*** type. When you are referred to a feature on a screen, the information will be **Bold and underlined**. Any mouse clicks are left-mouse button clicks unless otherwise noted. This is summarized below:

Type Face	User Action
Bold and Italic	The user is required to enter this information
Bold and Underlined	The user is directed to look for this feature in the program windows
Click	Left-mouse button
Right-Click	Right-mouse button

The Tour Starts Here...

We begin by starting the OLI Studio Program. This may be accomplished by ***clicking*** on the OLI Studio icon or by using the Start button and finding OLI Studio under *Programs*.

Once started, the OLI Splash screen will appear momentarily.

After a few moments, the main OLI Studio window will appear.

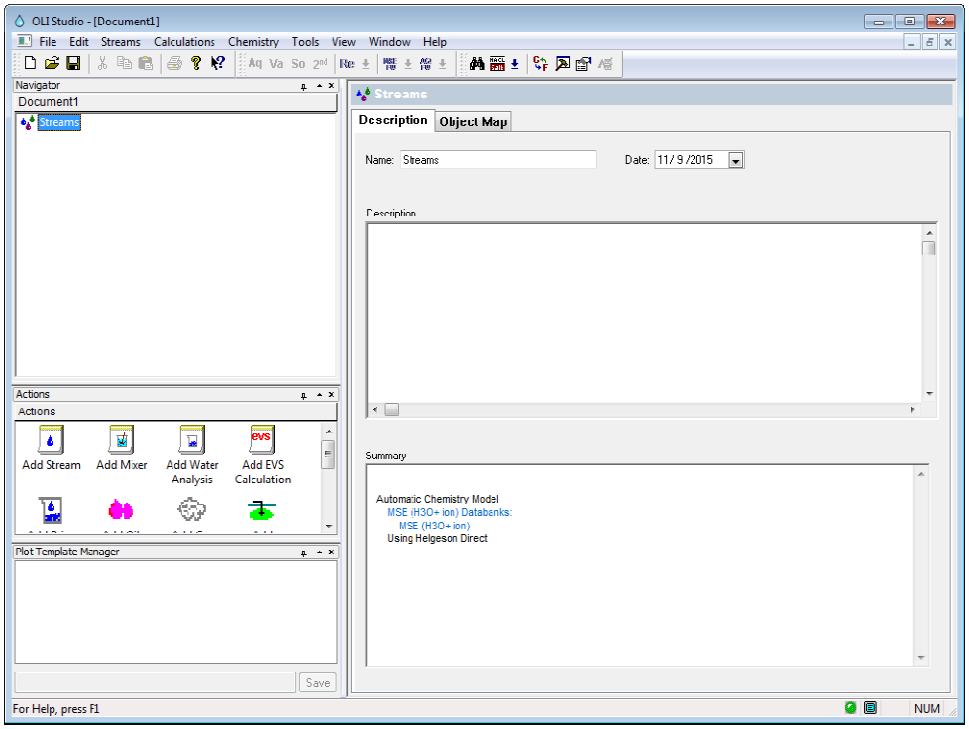


Figure 3-1 The OLI Studio main window

We now need to define the wastewater stream.

Scenario 1: Wastewater without additives

Step 1: Add the Stream

Click on the **Add Stream** icon**.** This will display the **Definition** window.

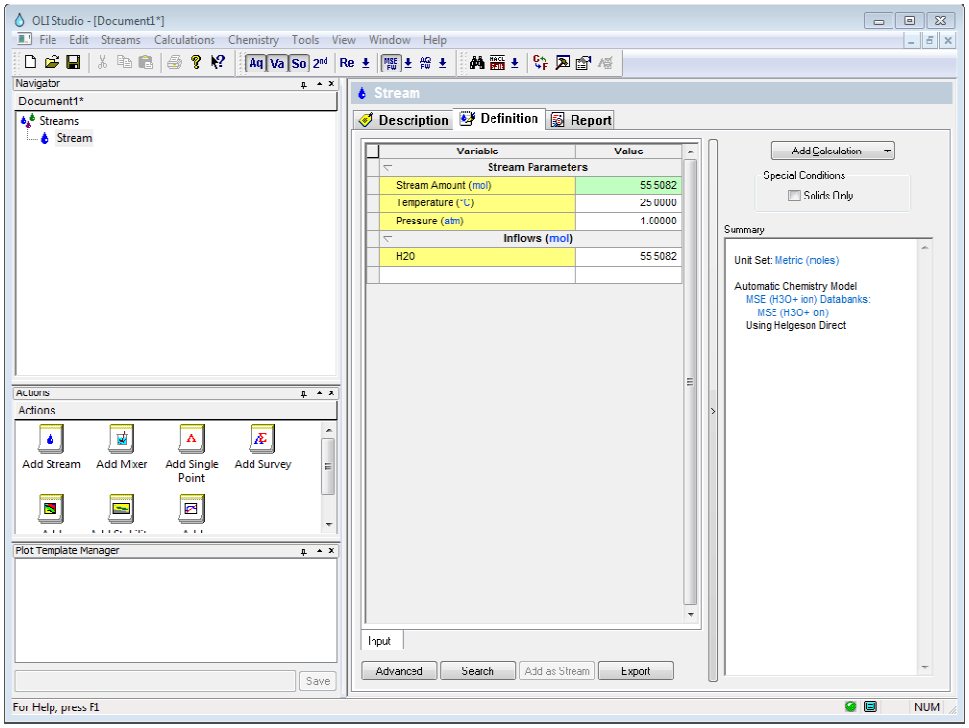


Figure 3-2 The streams definition view.

We should add some descriptive information about this stream so we can later identify the stream.

Step 2: Adding definitions

Click on the **Description** tab**.** This will display the description information

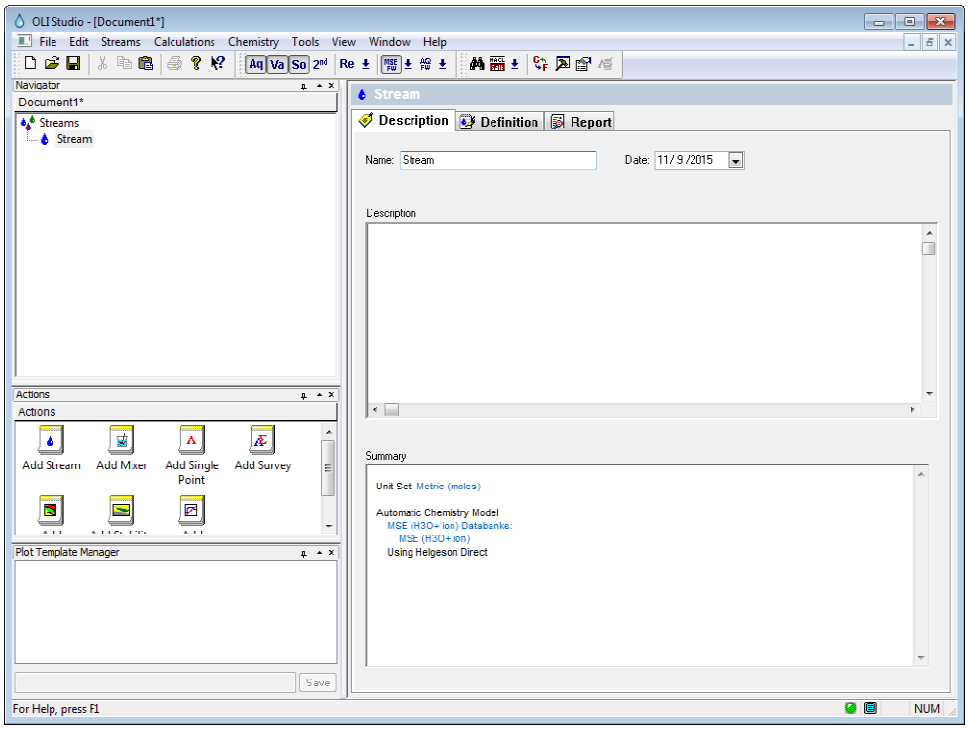


Figure 3-3 The Stream Description tab.

It is advisable to change the name of the stream from the default name. You may be entering many streams and will need to sort them out at a later time.

Step 3: Enter Stream Names and Definition

Replace the name ***Stream*** with the name ***Nickel Waste.***

Add the following text to the description box: "***Nickel waste water for the OLI Aqueous modeling Course."***

The summary box will contain additional information as the calculations proceed. This information maybe the name of additional databases or chemistry models imported from other OLI software packages.

The filled out windows will look like the following figure:

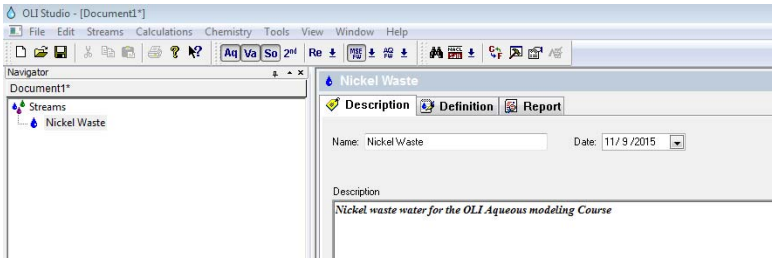


Figure 3-4 The filled out description window

Click on the **Definition** tab.

Step 4: Enter component inflows

Click in the white box in the grid below the **Inflows** line.

Add the formula ***$Ni(OH)_2$.***

Click in the white box next to the species you just entered and enter the value ***0.002.***
Press <Enter> to update the list.

After entering the values, the grid should look like the following:

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3

Figure 3-5 The filled out grid, notice the name Ni(OH)2 changed.

OLI Studio will automatically change the name of the species to the selected display name. In this instance, the name you entered was ***$Ni(OH)_2$*** but it may have changed to a different form. If it changed you can specify which display system to use in the following optional steps.

Optional

The default display name can be changed using a Menu Item called

Tool | Names Manager.

Step 4a: Select Tools from the Menu

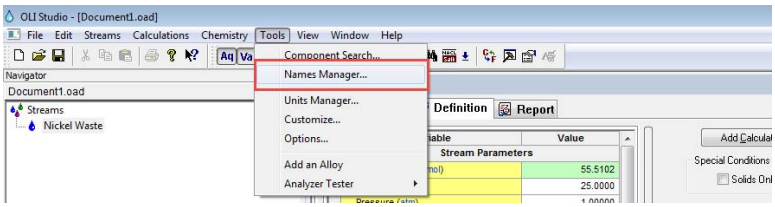


Figure 3-6 the Tools Menu

Select **Names Manager** from the Tools list.

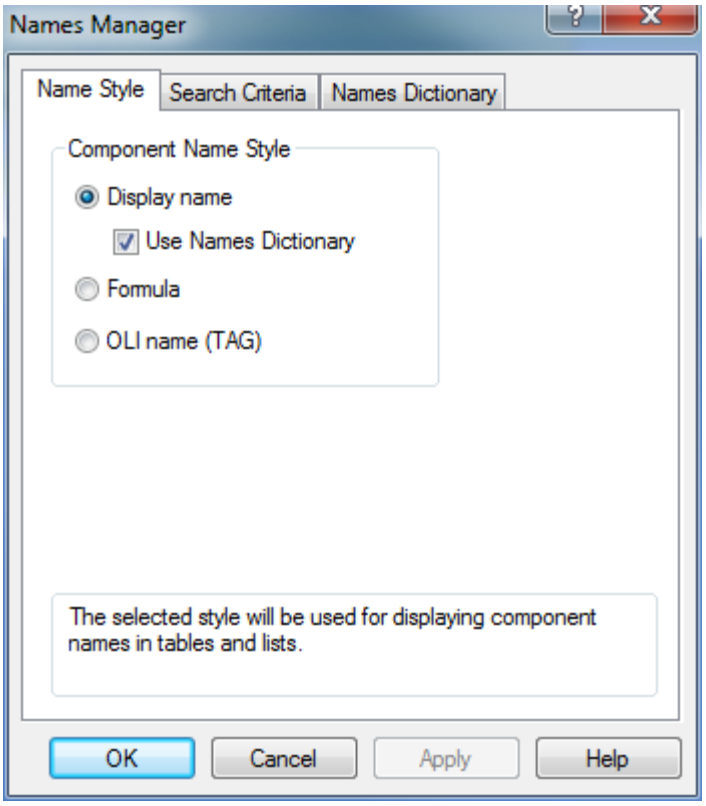


Figure 3-7 The Names Manager

The components can be displayed using the **Display Name** (default) or by the **Formula Name**. Alternatively, the traditional OLI Tag name[6] can be used.

Select the **Formula** radio button.

Click on the **Apply** button.

Click on the **OK** button.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3

Figure 3-8 The filled out grid in with formula names.

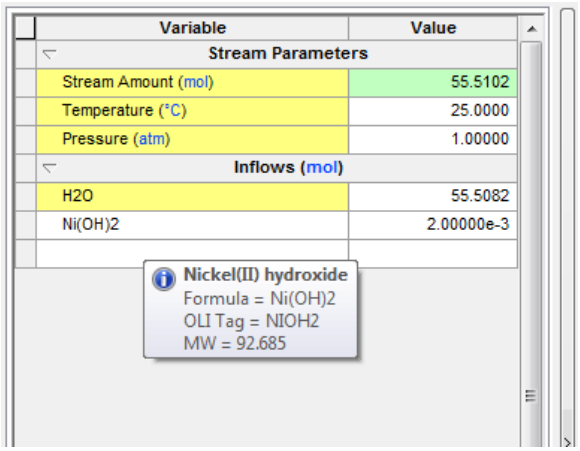
The remainder of this tour will use this name display system.

Now enter the 0.002 moles of $Ni(OH)_2$.

[6] This is also known as the ESP name.

We are now ready to begin the calculations. Our first task is to determine the pH of this solution.

OLI has added a new feature to the inflow grid. If you hover the cursor over the inflow components, you will see information about that particular chemical.



Step 5: Add a Single Point calculation to the Stream

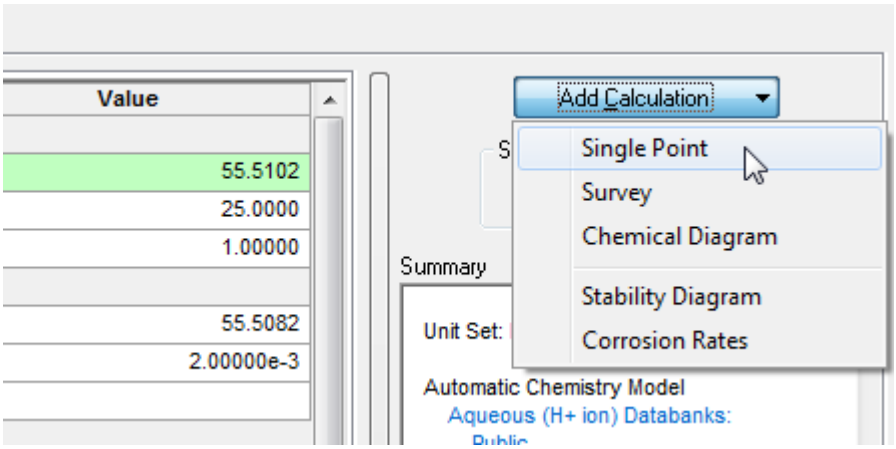


Figure 3-9 Selecting Single Point

Click on the ***Add Calculation*** Button and then select **Single Point.**

As with the stream definition, each calculation can have its own name and definition. We will add our definition for this calculation to remind us of what we did here. Click on the ***Description*** Tab.

Replace the Calculation name with ***Base Case pH.***

Add a description: ***Base Case pH without additives.***

The summary box will update with the status of the calculation. The following window shows this information.

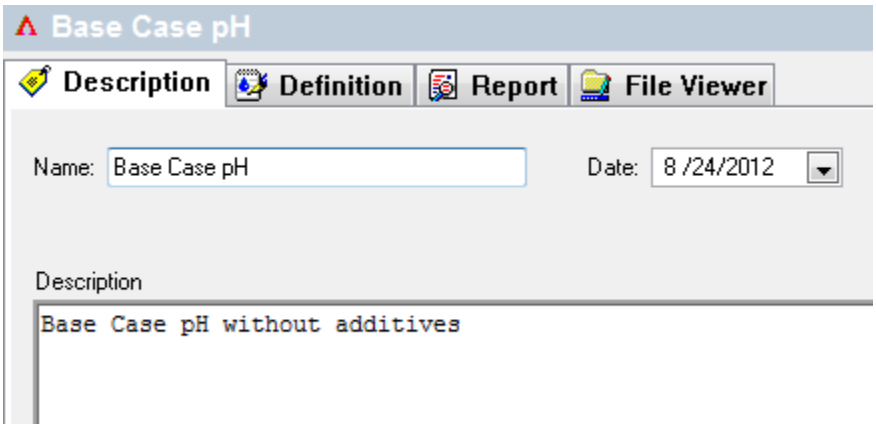


Figure 3-10 The filled out description

We can now start the calculation.

Click on the **Definition** tab.

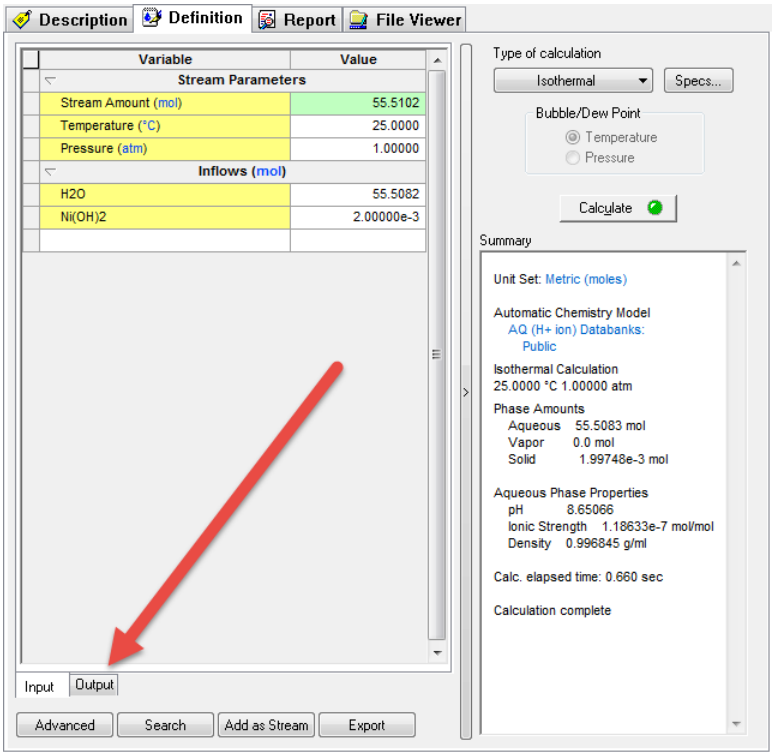
The information on this page does not need to be changed Please refer to Chapter 2 for additional information about the features on this page.

Click on the **Calculate** button.

When the program is completed (the orbiting ***e*** stops) we are ready to review the results. This may be done in several ways. This tour will examine several of the methods.

Step 6: Obtaining results

Click on the **Output** tab.



Next right-click anywhere in the gray field to display a pop-up menu.

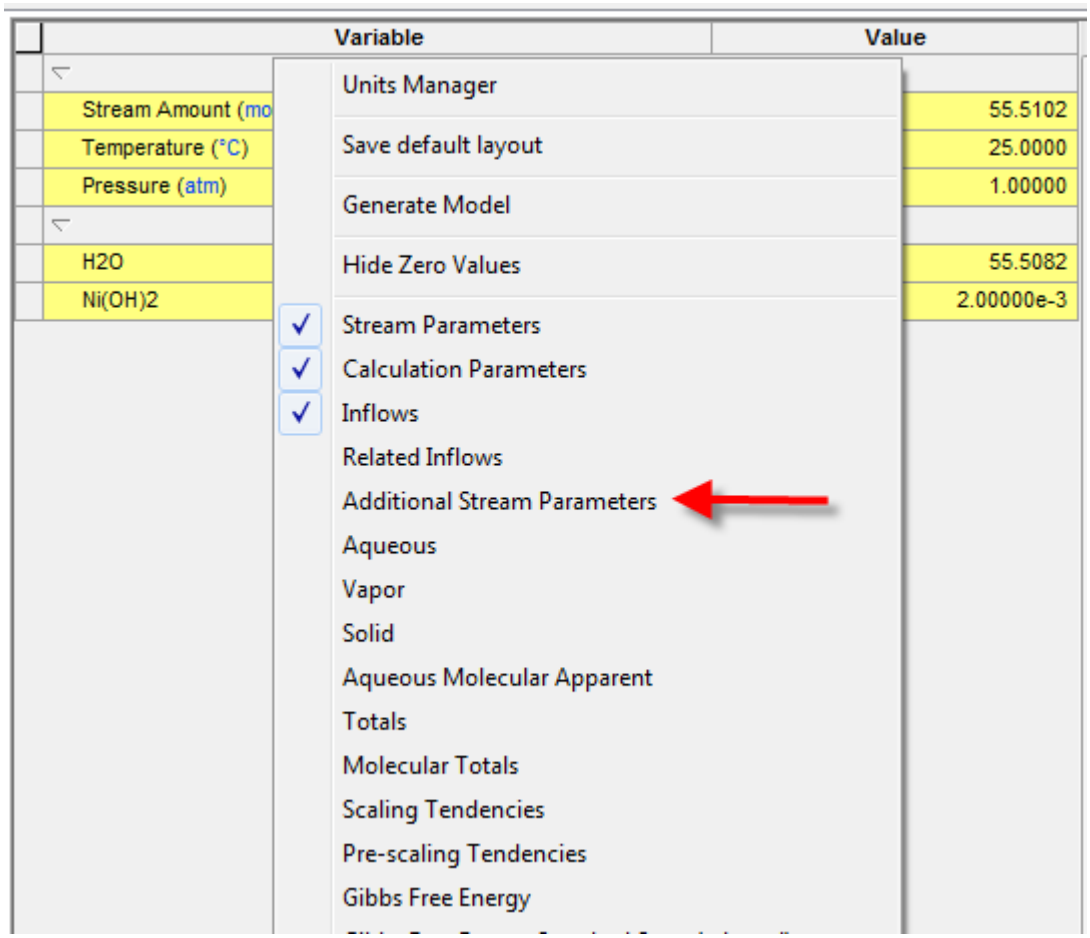
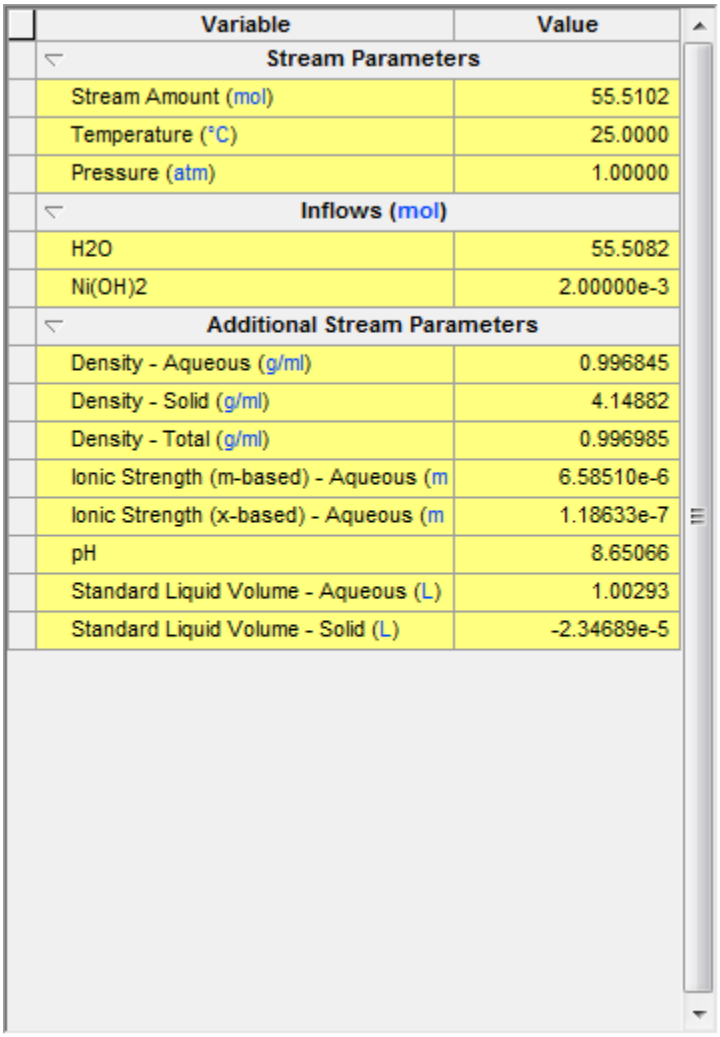


Figure 3-11 the advanced button

Select **Additional Stream Parameters.**

The grid will now change to yellow cells to indicate that these are calculated values. The pH can be found in the grid.



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5102
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3
Additional Stream Parameters	
Density - Aqueous (g/ml)	0.996845
Density - Solid (g/ml)	4.14882
Density - Total (g/ml)	0.996985
Ionic Strength (m-based) - Aqueous (m	6.58510e-6
Ionic Strength (x-based) - Aqueous (m	1.18633e-7
pH	8.65066
Standard Liquid Volume - Aqueous (L)	1.00293
Standard Liquid Volume - Solid (L)	-2.34689e-5

3-12 Scroll down to see more data if necessary

The pH is approximately 8.65. Your value may be different if the version you are using is more recent than the version used to create this manual.

Our primary interest in this application is finding the optimum pH for nickel removal. To create a plot of the data, we will need to make a survey.

Step 7: Adding a pH Survey

There are many ways to move around in the OLI Studio. We will constantly highlight them as we move around in the tours. Remember that there is frequently more than one method to achieve a desired result.

Click on the **Nickel Waste** icon in the tree view on the left-hand side of the window.

This will bring you back to the top of the series of calculations by displaying just the stream information.

Click on the **Add Calculation** button and select **Survey.**

You can now add descriptive information about this calculation. We recommend the following (please note: We will only display windows that require new explanations)

Enter a new Survey name of **Base Survey.**

Enter a Description: ***Base pH survey without additives.***

Click on the **Definition** tab.

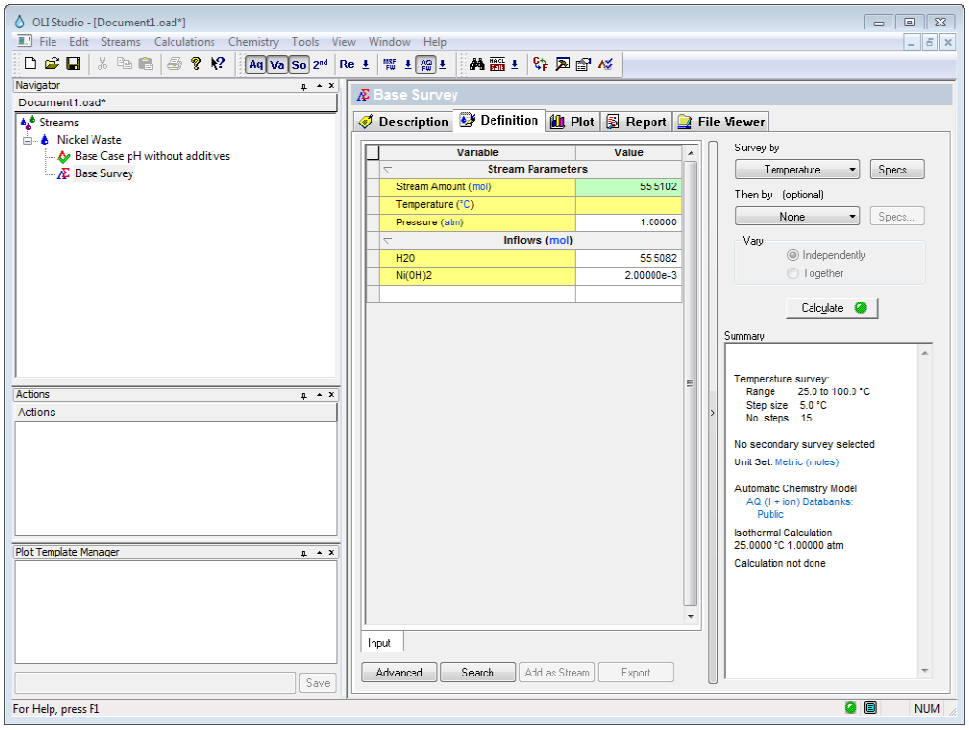


Figure 3-13 The Default Survey Definition Tab.

Since we do not want a temperature survey which is the default, we will need to change the survey type.

Click on the **Survey by** button and then select **pH.**

The calculate button light is red which indicates that the calculation is not yet ready to proceed. The Summary box indicates that we require additional information.

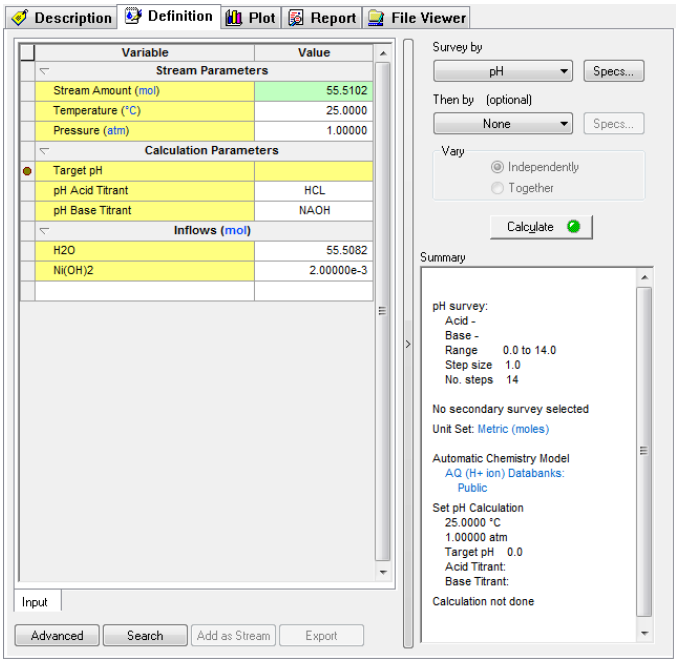


Figure 3-14 Survey Summary (Default Values)

The default acid titrant and the base titrant are already defined (HCl and NaOH.)

We are now ready to begin the calculations.

Step 8: Save, save, save!!!

We should now save our work. It is very frustrating to work for a long period of time and forget to save our work.

We will recommend that you save the name of the file as **OLI AQ Course**. Of course, you may use any name you want. We also recommend that you create a working folder and save the file there. We will create a folder named **OLI Calcs.**

Select **File** and then **Save As** from the menu.

Step 9: Ok then, we're ready to continue

Click on the **Calculate** button.

The program will run for a short time. When the orbit disappears, check the summary box to see if the calculation is complete. In the tree-view, you can expand the survey to see if all the points converged.

A small calculation result window may appear. If it does, simply close it.

Step 10: Obtaining results

We can now obtain some graphical results.

Click on the **Plot** tab.

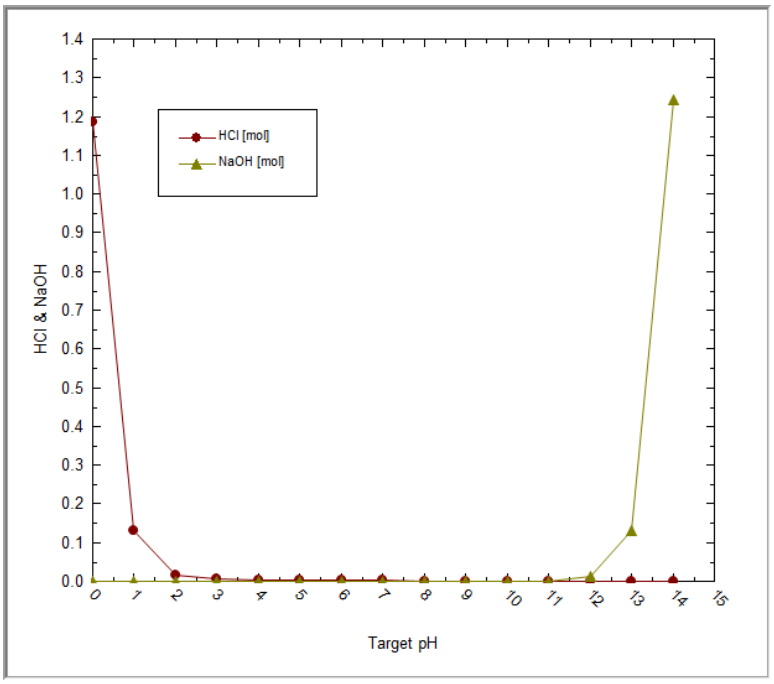


Figure 3-15 the default plot

For many calculations, the values on the plot extend over a very large range of numbers. The default linear axis may not capture all the details we require.

Right-click anywhere in the plot window and select **Plot Options**

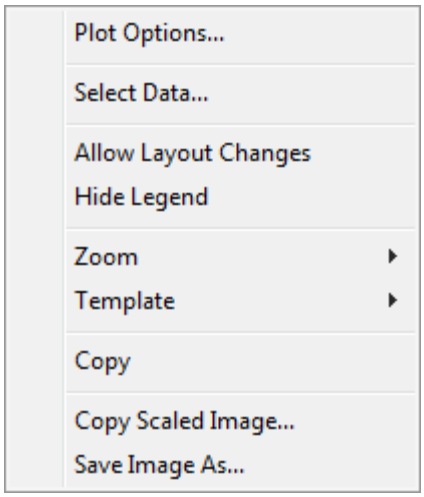


Figure 3-16 the plot right-click

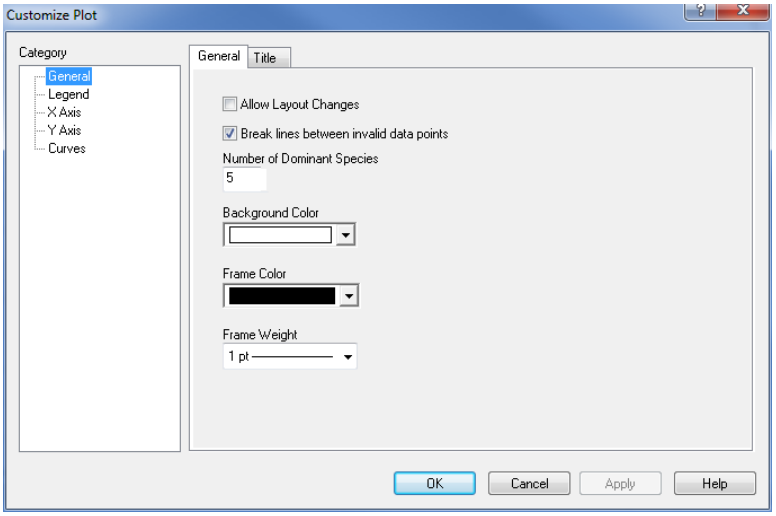


Figure 3-17 Plot Options

Select Y-Axis from the Category List.

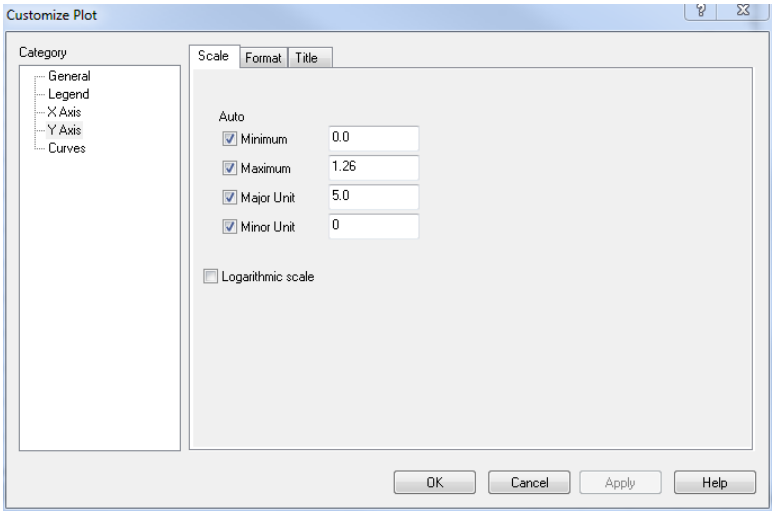


Figure 3-18 Setting log for Y-Axis

Check the **Logarithmic Scale** Box and then **Click** on the **OK** box**.**

The display will now change.

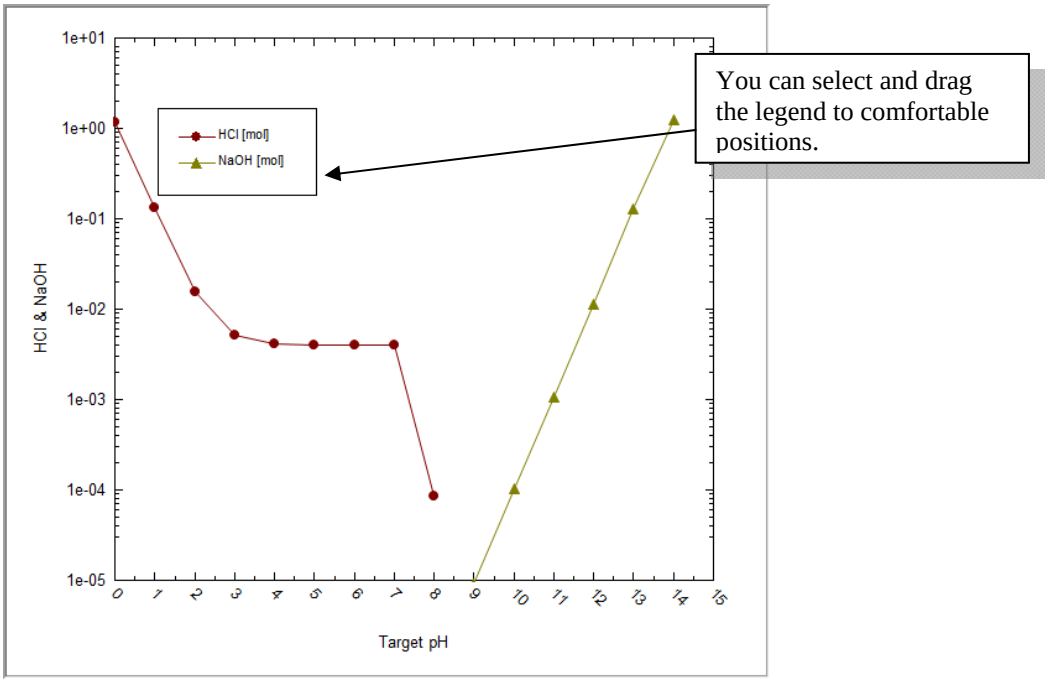
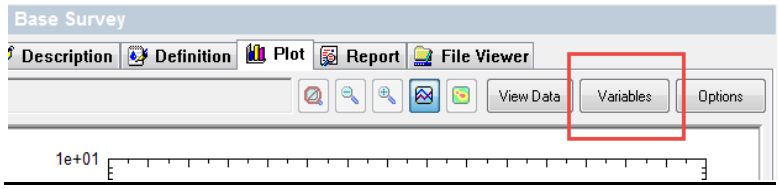


Figure 3-19 log axis plot

Although this plot tells us a great deal, we require more specific information about nickel species. Remember, there is a limit to the amount of soluble nickel that can be discharged. We need to clean this diagram up.

Click on the **Variables** button.



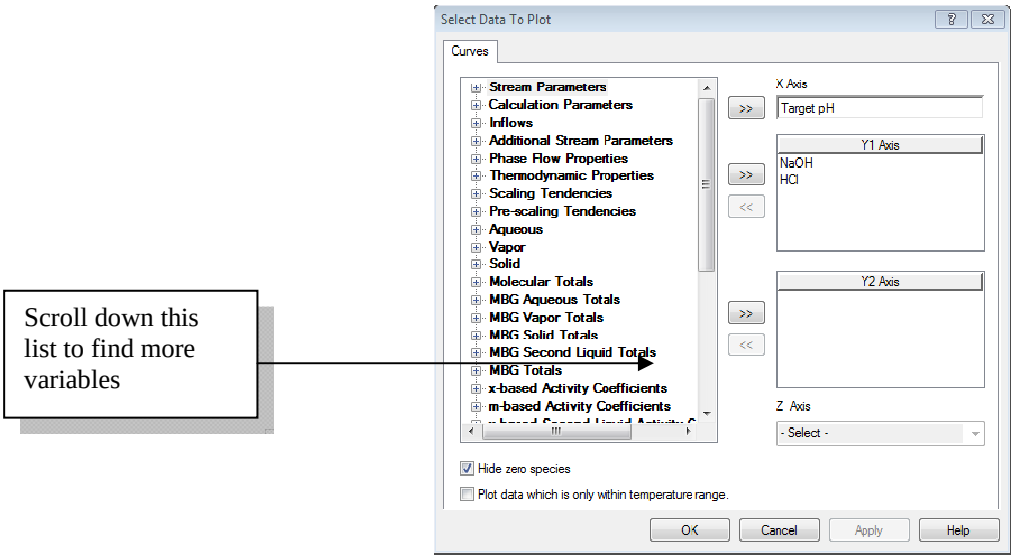


Figure 3-20 The curves plot dialog

The **NaOH and HCl** variables in the **Y-Axis** box should be displayed. Select them and then ***Click*** on the left **double-arrow (<<)** button which will remove it from the plot.

Scroll down the left-hand window to find **MBG Aqueous Totals** and expand the list by clicking the small "+" icon.

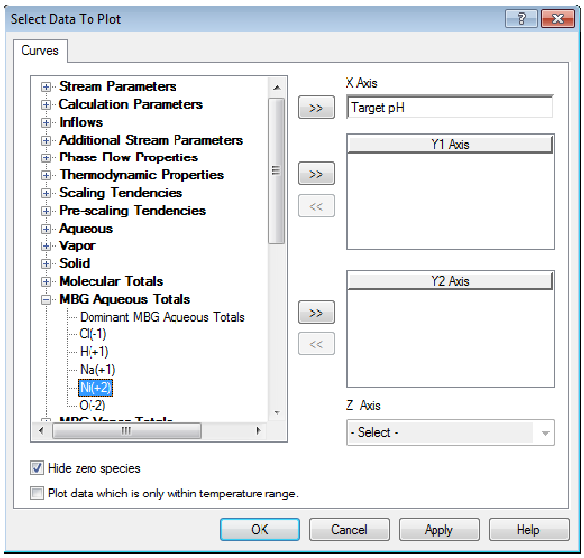


Figure 3-21 Selecting more variables

MGB is an abbreviation for Material Balance Groups

The grid updates to show the material balance totals available to display. In this case we desire the Nickel (+2) species. The variable displayed will be the sum of all nickel containing species in the aqueous phase.

Double-Click the **NI(+2)** item or select it and use the **>>** button. ***Click*** on the **OK** button.

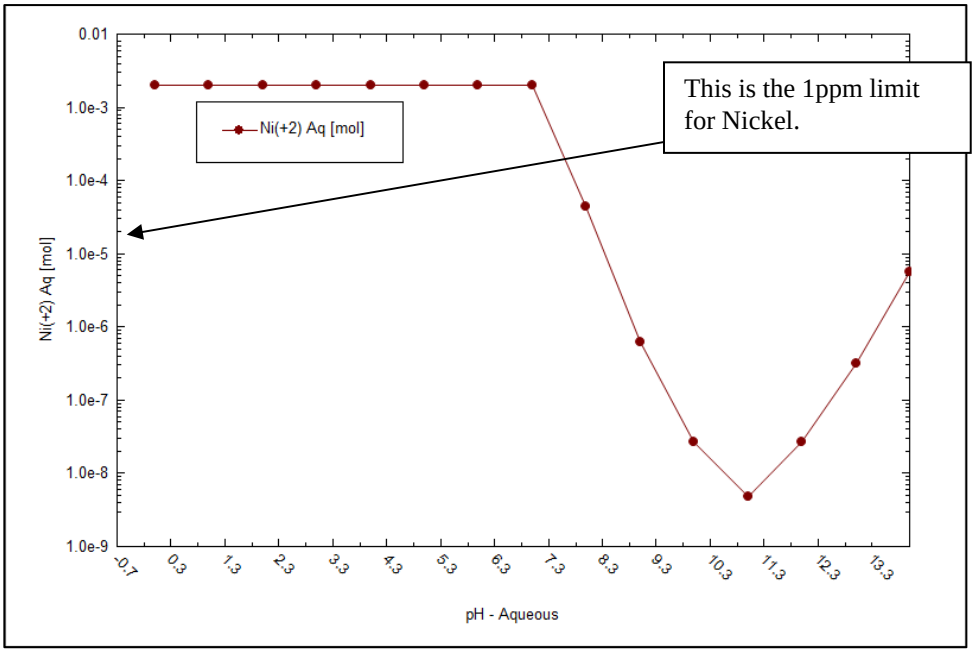


Figure 3-22 The results of the pH survey.

The material balance group variable is a sum of all the species for that material in the phase requested. For example, in this case all the NI(+2) –Aq variable is a sum of all nickel containing ions in solution. Any solids are excluded.

You can see that a minimum in aqueous solubility seems to occur in the pH=11 range. This is the result of nickel solids forming and leaving the aqueous phase.

The limit of 1 ppm for Ni^{+2} is approximately 2 x 10^{-5} moles. At a pH=10, we are several orders of magnitude below this limit.

What else is important in this solution?

Click on the* Variables *button and add the following species to the plot (you may need to scroll up or down to find all the species).

Aqueous:

Ni(OH)2

NiOH+1

Ni+2

Ni(OH)3-1

Solids:

Ni(OH)2

Click on the ***OK*** button when done.

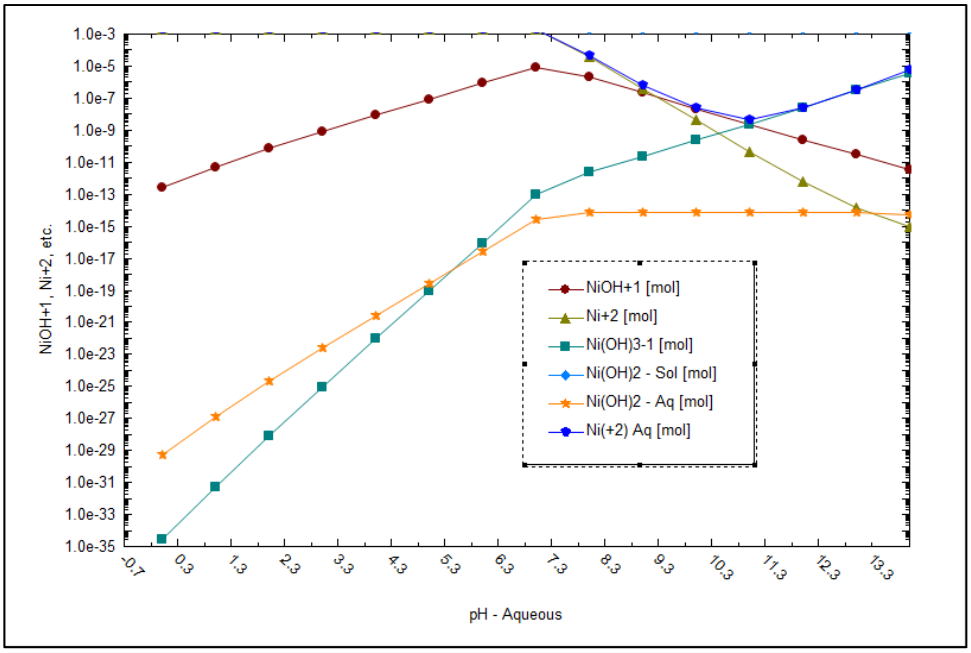
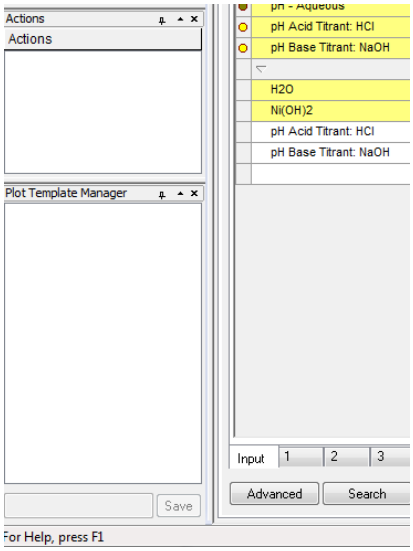


Figure 3-23 Important nickel species

You can see that the soluble nickel (Ni(+2)-Aq) is a summation of the other species. The large drop in the value is because most of the nickel leaves the aqueous solution as Ni(OH)2-Solid at pH's greater than 7.0 with a maximum near pH=11.

Plot Template Manager:



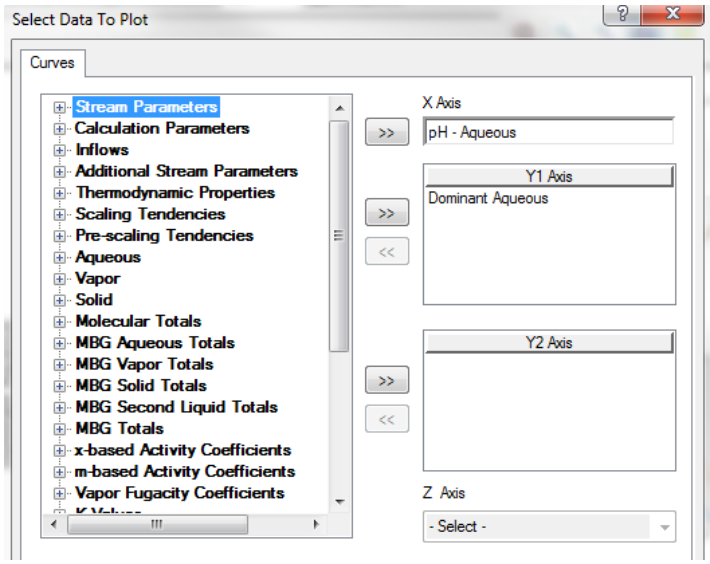
This newly added tool in OLI software is designed to help users save their most frequent plots. For example you may not want to always look at the dominant Aqueous plot vs. pH in all cases. For example, if you are always using nickel chemistry you can have a custom plot available. To create this template please follow the steps:

1. Create the case with desired chemistry and inflows

2. Add a survey depending on type of calculation

3. Customize the survey to your everyday parameters you are interested in, like mass/solids/MBG totals etc

Basically it could be any combination form the list below:

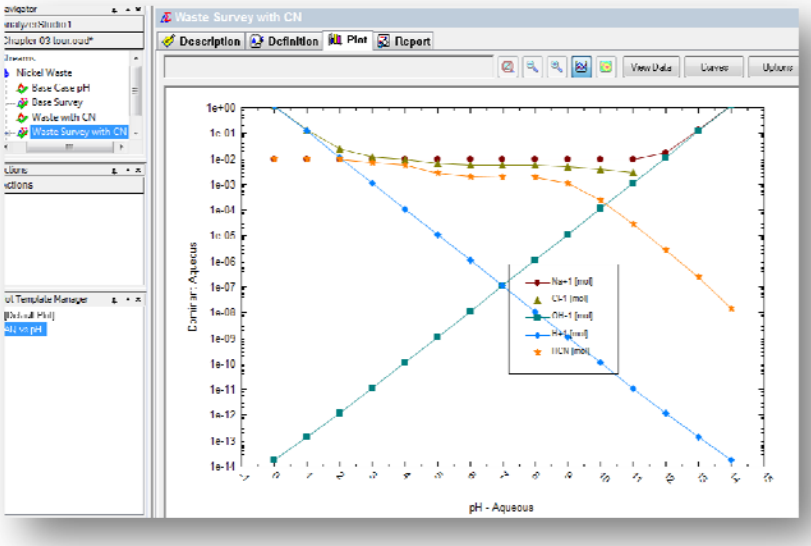


Right now it is set to the above mentioned example, Dominant Aqueous vs pH.

Save the description in the left hand corner panel named Plot Template Manager. AQ vs pH is the name in this case.

Hit save. Now here are two plots on that list now. First is default and second is AQ vs pH. You are now able to see these plot conditions for any other analyzer object in this case when you add survey for that object.

Go to a different case which already has a survey.



As you can see, AQ vs pH plot is selected (there is a cursor hovering above it) and the graph looks like above. If you click on the option instead of hovering over, this look of the plot gets saved for those conditions, and you will see this template every time you open the case.

Scenario 2: Now, What about the Real Waste?

The real importance of aqueous speciation modeling of this treatment is only really appreciated if we introduce the cyanides, which brings us to the real waste treatment problem.

For this scenario, you will repeat many of the same steps as in the first scenario. We recommend that you create new calculations below the **Nickel Waste** stream. This will keep the core composition the same without affecting the results of other calculations.

Please follow these steps for this next scenario. Please note: we will only show the screens that are substantially different from those that you have scene.

Step 1: Add a new Single Point calculation

***Click on the* Nickel Waste *stream in the* Tree view.**

This will display the **Actions** pane in the bottom left corner of the OLI Studio window.

Click on the **Add Single Point** icon in the **Actions** pane.

Change the ***Name*** and ***description:***

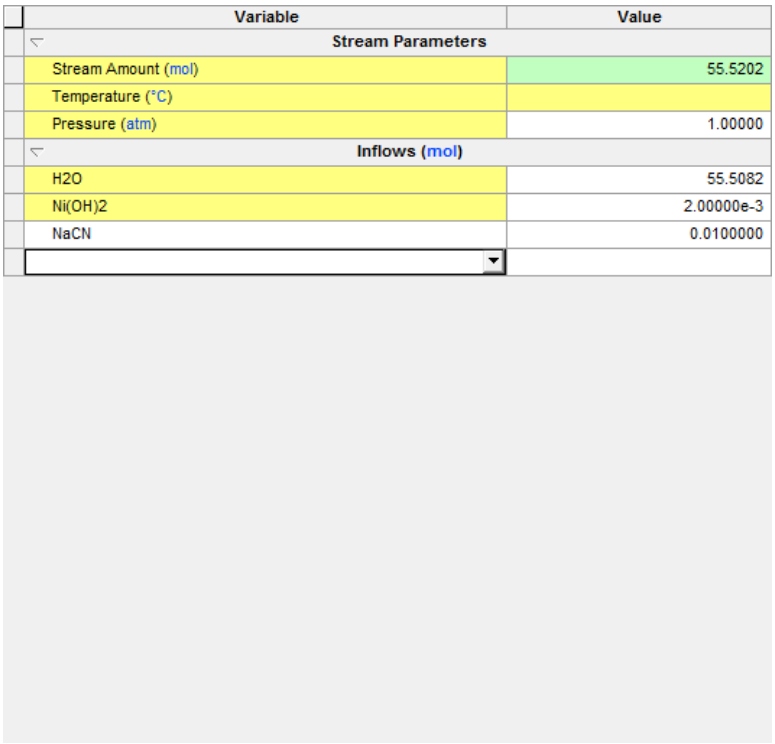
Name: ***Waste with CN.***

Description: ***Nickel waste with cyanide added.***

Click on the **Definition** tab.

Add **NaCN** to the grid and a value of 0.01 moles.

The grid should now look like this:



Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5202
Temperature (°C)	
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3
NaCN	0.0100000

Figure 3-24 Adding NaCN

When the <u>Calculate Button</u> light turns green, Click on the button.

Step 2: Getting results of the Single Point Calculation.

Next locate the **"Output"**mini-tab at the bottom of the definition:

Right-click anywhere in the grid.

The following pop-up menu will appear.

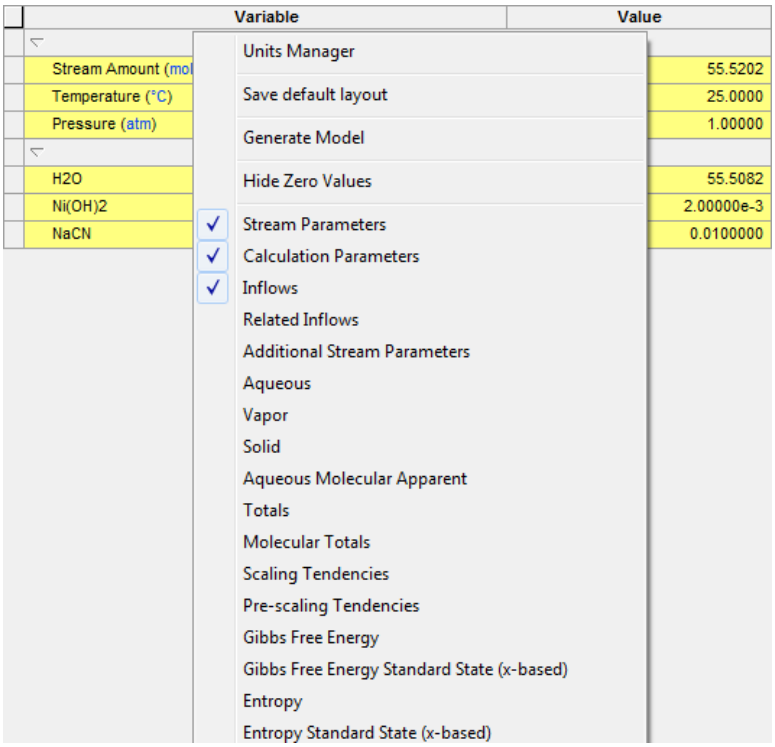


Figure 3-25 Right-clicking on the grid

Select **Additional Stream Parameters.**

The resultant pH should be approximately 11.6.

Variable	Value
Stream Parameters	
Stream Amount (mol)	55.5202
Temperature (°C)	25.0000
Pressure (atm)	1.00000
Inflows (mol)	
H2O	55.5082
Ni(OH)2	2.00000e-3
NaCN	0.0100000
Additional Stream Parameters	
Density - Aqueous (g/ml)	0.997132
Density - Total (g/ml)	0.997132
Ionic Strength (m-based) - Aqueous (m	0.0120000
Ionic Strength (x-based) - Aqueous (m	2.16114e-4
pH	11.5484
Standard Liquid Volume - Aqueous (L)	1.00334

Figure 3-26The pH = 11.5484 which is close to 11.6

Step 3: Setup and run the pH survey.

Click on the **Nickel Waste** stream in the **tree view** in the left-hand window.

This will display the **Actions** pane in the bottom left corner of the OLI Studio window.

Click on the **Add Survey** icon in the **Actions** pane.

Click on the **Description Tab.**

Enter a New name: ***Waste Survey with CN.***

Enter a Description: ***pH survey with both Nickel and CN.***

Click on the **Definition Tab**

Add ***NaCN*** to the grid with a value of ***0.01*** moles

Click on the **Survey By** button and select pH.

(HCl and NaOH are the default titrants and are automatically added)

Click on the **OK** button.

Click on the **Calculate** button.

Step 4: Reviewing results.

Review the steps in **Scenario 1: Step 10** on page 3-44. We wish to plot the following variables, remove any variables that we don't want:

1. The material balance group aqueous for Ni(+2)
2. Aqueous Species: Ni(CN)4-2

3. Aqueous Species: Ni+2
4. Aqueous Species: NiOH+1
5. Aqueous Species: Ni(OH)3-1
6. Aqueous Species Ni(OH)2
7. Solid Species: NiNi(CN)4-Solid

Toggle the view to Y-axis log. The plot should look like this:

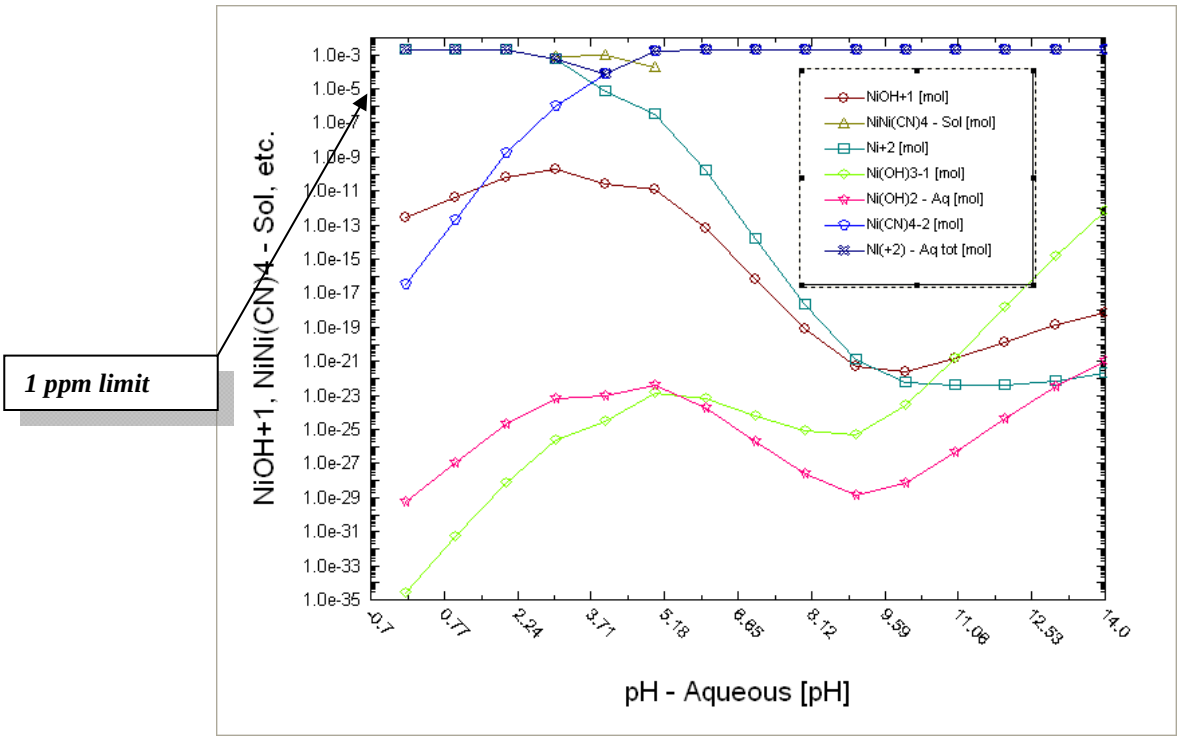


Figure 3-27 Nickel Waste Stream with NaCN added

The results have changed very dramatically. The new optimum pH for Ni removal is around 4.0, rather than 10.0. The lowest total Ni remaining in solution is now on the order of 10^{-4} which is actually well over 1 ppm.

The culprit is the $Ni(CN)_4^{-2}$ complex of nickel and cyanide. Basically, the plot of the total Ni in solution and the $Ni(CN)_4^{-2}$ complex overlap over the interval pH=5 to 12. This means that virtually all nickel in solution is in the form of this complex.

This complex thus holds the Ni in solution and does not allow the nickel hydroxide to even form. Instead, a much weaker precipitate, the $NiNi(CN)_4$ salt forms over a narrow range of pH with 4.0 being the optimum.

Scenario 3: Is All Really Lost?

We can now make an attempt to influence nature by introducing a source of sulfide. We do this because nearly all metal sulfide salts are highly insoluble.

Create a new single point calculation and survey as you did in the previous two scenarios.

Add ***0.01*** moles of ***NaCN***

Add ***0.01*** moles of ***H2S***

Plot the following variables when the calculations are complete**:**

1. The material balance group aqueous for Ni(+2)
2. Aqueous Species: Ni(CN)4-2
3. Aqueous Species: Ni+2
4. Solid Species: NiS-Solid

Toggle the view to Y-axis log. The plot should look like this:

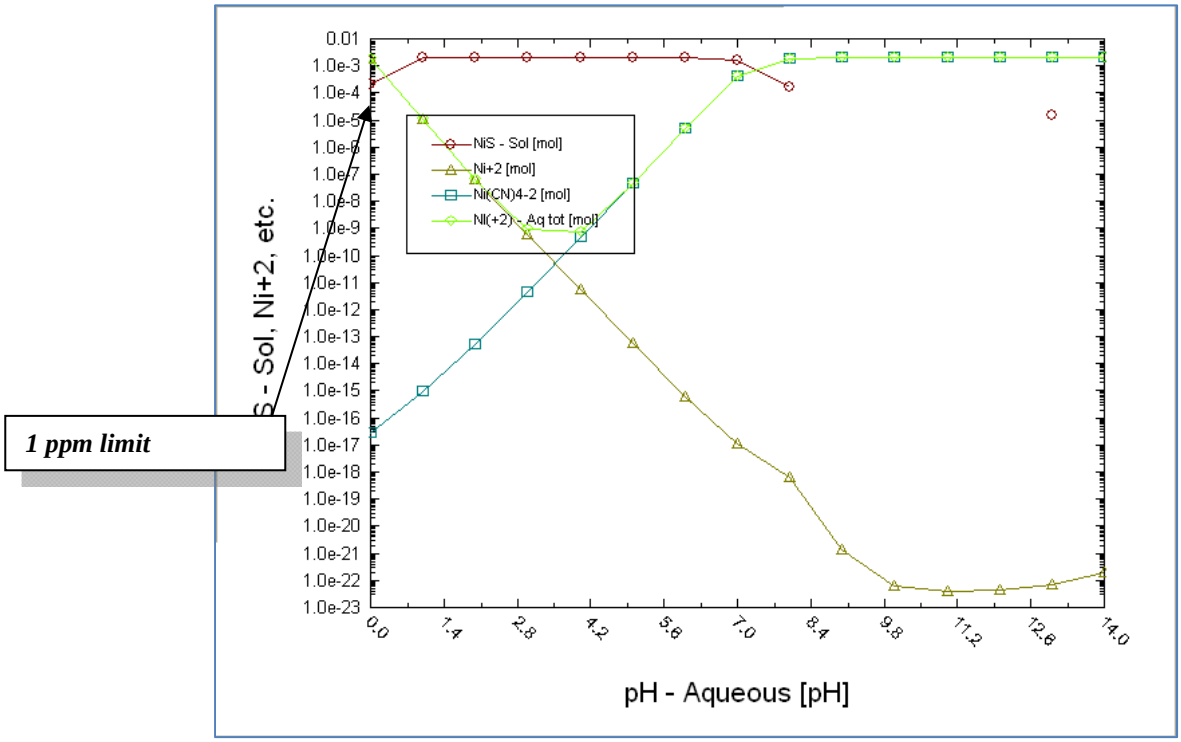


Figure 3-28 Waste Stream pH with both NaCN and H2S added

The results reflect a "power struggle" between the $Ni(CN)^{-2}$ which is holding the nickel in solution and the NiS solid which clearly has a greater tendency to form than the $NiNi(CN)_4$ solid. As a result, our optimum pH is still around 4.0 and we are now around 10^{-5} total nickel in solution which is a bit below 1 ppm.

Final Thoughts...

Aqueous speciation modeling can teach us a great deal about complex chemical systems and the interactions of individual species.

The actual removal achieved with sulfide may not be quite enough to satisfy the regulators. This in itself is useful information to have. In addition, with the power of OLI Studio, one could now explore alternative treatment methods such as ion exchange.

Although such a simulation is beyond the scope of the tour, consider how vital it is to know that the dominant species to be exchanged (removed from solution) is an anion $Ni(CN)^{-2}$ and not the cation (Ni^{+2}) as the conventional wisdom might dictate.

Save, Save and then Save again

This would be a good time to save your work. You may use the File/Save As… menu item or use the Save icon on the toolbar.